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A Sensitive Phonon-Based Probe for Structure Identification of 1T' MoTe₂

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Supporting Information Placeholder

ABSTRACT: In this work, by combining transmission electron microscopy and polarized Raman spectroscopy for the 1T' MoTe₂ flakes with different thicknesses, we found that the polarization dependence of Raman intensity is given as a function of excitation laser wavelength, phonon symmetry and phonon frequency, but has weak dependence on the flake thickness from few-layer to multilayer. In addition, the frequency of Raman peaks and the relative Raman intensity are sensitive to flake thickness, which manifests Raman spectroscopy as an effective probe for thickness of 1T' MoTe₂. Our work demonstrates that polarized Raman spectroscopy is a powerful and nondestructive method to quickly identify the crystal structure and thickness of 1T' MoTe₂ simultaneously, which opens up opportunities for in-situ probing anisotropic properties and broad applications of this novel material.

MoTe₂ has recently attracted enormous interests due to its novel physical properties¹⁻³ and promising applications in electronics, optoelectronics, photovoltaics, valleytronics and spintronics, etc.⁴⁻⁷ MoTe₂ can crystallize in four different phases: 2H phase (hexagonal structure), 1T' phase (monoclinic structure), T_d phase (orthorhombic structure) and 1T (octahedral structure).⁸⁻¹¹ Since the energy difference between semiconducting phase 2H and semi-metallic phase 1T' MoTe₂ is small compared with other transition metal dichalcogenides (TMDs),¹² MoTe₂ with various phases can be directly synthesized by tuning growth parameters (precursors, temperature, cooling rate etc.).^{8,10,11} Laser patterning⁴ and strain engineering¹³ techniques have been suggested as ways to realize semiconducting-semimetallic phase transition of MoTe₂. While the studies of other TMDs mainly focus on the semiconducting phase, the semimetallic phases of MoTe₂ (1T' and T_d) have attracted much attention and possess potential applications in quantum computing.^{1-3,5} 1T' MoTe₂ has been observed to transfer to T_d MoTe₂ through temperature-

induced phase transition when cooling down below 240 K.² The low-temperature phase T_d MoTe₂ is a type-II Weyl semimetal, which exhibits novel quantum properties such as topological surface state Fermi arcs, chiral anomaly-induced negative magnetoresistance, etc.² Moreover, pressure-driven superconductivity³ and large magnetoresistance¹ were observed in 1T' MoTe₂. Besides these remarkable properties, the low-symmetry crystal structure may lead to several anisotropic properties in 1T' MoTe₂. However, few works have addressed this topic because the crystal can be readily degraded in the air and the characterization for the specified structure is not straightforward. To investigate the relationship between anisotropic properties and crystal structure of 1T' MoTe₂, a sensitive, reliable and non-destructive method to determine the crystal orientation is highly desirable.

Besides anisotropy, the thickness of 1T' MoTe₂ also strongly affects its properties. In contrast to the semi-metal bulk 1T' MoTe₂, few-layer 1T' MoTe₂ has an energy band gap opening because of the strong spin-orbit coupling.¹ Monolayer 1T' MoTe₂ is predicted as a class of large-gap quantum spin Hall insulators, and can be used as the key material in the topological field effect transistor, which uses topological phase transition to realize fast on/off switching.⁵ Moreover, the 1T' MoTe₂ samples with odd number of layers have inversion symmetry, while the inversion symmetry is broken for even number of layers.¹⁴ Since monolayer and few-layer 1T' MoTe₂ easily degrade in air, direct measurement of the thickness using atomic force microscopy (AFM) is impractical. Therefore, it is of great importance to develop a non-destructive, convenient method to probe the thickness of 1T' MoTe₂.

In this work, we have investigated the polarization dependence of 1T' MoTe₂ with various thickness using polarized Raman spectroscopy with different excitation laser wavelengths (532, 633 and 785 nm). In particular, we performed transmission electron microscopy (TEM) on 1T' MoTe₂ and correlate it with polarized Raman results. The combination of select area electron diffraction (SAED), TEM and high

angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging and polarized Raman spectroscopy for the flakes of 1T' MoTe₂ with different thickness reveals the relationship between crystalline orientation and Raman intensity as a function of excitation laser wavelength, phonon mode and phonon frequency. Moreover, it was found that polarization dependent Raman spectroscopy can also be effective in determining the thickness of 1T' MoTe₂. Our work demonstrates that polarized Raman spectroscopy can be used as a powerful and nondestructive method to identify the crystal structure and thickness of 1T' MoTe₂ simultaneously, which opens up opportunities for in-situ probing anisotropic properties of 1T' MoTe₂.

Bulk 1T' MoTe₂ belongs to the space group P2₁/m. As illustrated in Figure 1a and 1b, the monoclinic structure of 1T' MoTe₂ consists of a shifted Mo atom from the center of Te octahedron and the Mo atoms form the in-plane Mo-Mo bonds, resulting zigzag Mo chains along the [010] (y)-direction. The in-plane Mo-Mo bonds distort the Te octahedral plane, and form the monoclinic structure.¹⁵ The HAADF-STEM image of the exfoliated 1T' MoTe₂ flake (Figure 1c) confirms the monoclinic structure and high quality of the bulk 1T' MoTe₂ crystal and exfoliated 1T' MoTe₂ flakes.

The phonon modes of 1T' MoTe₂ were investigated using polarized Raman scattering in the parallel configuration (the polarization of the scattered light is parallel with the polarization of incident light). Bulk (monolayer) 1T' MoTe₂ have 36 (18) vibrational modes, and 18 (9) of them are Raman active from group theory. There are a total of 12 (6) A_g modes and 6 (3) B_g modes for bulk (monolayer) 1T' MoTe₂. The calculated frequencies of the 18 (9) Raman modes are listed in Table S1(2). The typical polarized Raman spectra of a 1T' MoTe₂ (5-7 nm thick) flake under different laser wavelengths (532, 633 and 785 nm) and different polarized angles (0°, 45°, and 90°) are shown in Figure 1d. In this paper, we define 0° as the [010] (y) crystal orientation, 90° as the [100] (x) orientation. The peak intensity for 1T' MoTe₂ reveals strong dependence on excitation laser wavelengths, and varies dramatically with polarization angles, as seen in Figure 1d. The change of the Raman spectra with different polarization angles are due to the in-plane anisotropy of 1T'-MoTe₂. The number of modes changes with excitation laser wavelengths and polarizations, which is relevant to resonance Raman properties and the symmetry of the wavefunctions, respectively, as discussed below. For the Raman spectra excited by the 532 nm laser, there are 11 Raman peaks observed at 78, 94, 104, 111, 128, 163, 190, 252, 259, 265 and 279 cm⁻¹, among which 94, 104, 111, 190 cm⁻¹ modes correspond to the B_g Raman modes and the others correspond to A_g modes (see Table S1). The Raman spectra of the 633 nm laser shows fewer peaks, and the peaks at 190, 252, 279 cm⁻¹ did not appear. The number of Raman peak excited by the 785 nm laser is much fewer and only four peaks at 78, 163, 252, 265 cm⁻¹ were observed. This is due to the lack of resonance condition with increasing laser wavelength, as seen from Figure S2. The weakening electron-photon resonance condition from the 532 nm laser to the 785 nm laser leads to the weaker or even vanishing Raman peaks.

Moreover, the peak frequency and relative intensity also vary with excitation laser wavelengths. For example, for 0° polarization, the intensities of 163 and 78 cm⁻¹ modes are similar to those for the 532 nm laser, but the intensity of 163 cm⁻¹ mode becomes significantly smaller than that of 78 cm⁻¹

modes for 633 and 785 nm laser. Also, it can be observed that peaks under 633 nm laser is a little red-shifted compared to other lasers. In the following, we demonstrate how Raman spectra measured under various laser excitations can be useful for the practical application of MoTe₂ with two major aspects: determining the crystalline orientation and flake thickness.

Figure 1. (a-b) The crystalline structure of the bulk 1T' MoTe₂ from the perspective view (a) and top view (b). The red dashed lines in (b) denote a zigzag Mo chain. (c) HAADF-STEM image from the exfoliated 1T' MoTe₂ flake supported on a TEM grid. (d) Typical Raman spectra of a 1T' MoTe₂ flake measured under three excitation lasers and three polarization angles. For each polarization angle, the bottom, middle and top spectra are measured under 532, 633 and 785 nm laser excitations, respectively. (e) Calculated nonresonant Raman spectrum of bulk 1T' MoTe₂.

To probe the crystal orientation of 1T' MoTe₂, and investigate how it relates to anisotropic Raman spectroscopy in 1T' MoTe₂, SAED, TEM, HAADF-STEM and polarized Raman spectroscopy were performed on the same 1T' MoTe₂ flakes with various thickness. Figure 2a presents a typical optical microscope image of 1T' MoTe₂ flakes protected by TEM grid and PMMA layer. The corresponding SAED pattern of the 1T' MoTe₂ flake shows rectangular pattern (Figure 2b), which can be indexed with the monoclinic structure of the 1T' phase, and used to determine the crystal orientation on this specific flake. The corresponding HAADF-STEM image in Figure 2c matches well with the image simulation based on the 1T' MoTe₂ structure, shown in the inset of Figure 2c, which unambiguously points out the crystal orientation of the flake and verifies the high-quality of exfoliated flakes.

We measured the polarized Raman spectra and corresponding crystal orientation by TEM on 1T' MoTe₂ flake, presented in Figure 2d. It can be observed clearly that the peak intensities change with polarization angles in different ways. 7 Raman modes are observed, among which 5 are of A_g symmetry (78, 128, 161, 259, 265 cm⁻¹) and 2 are of B_g symmetry (94, 104 cm⁻¹) (Figure 2d). As shown in Figure 2e, the Raman polar plots correspond well to the crystalline orientation determined by TEM. The intensity of the four A_g Raman peaks at 78, 128, 259, 265 cm⁻¹ varies with a period of 180°,

and the maximum intensity appears at a specific polarization angle along with the [100] crystal axis. In contrast, for the A_g Raman peak around 161 cm^{-1} , the maximum intensity occurs when the polarization angle is along with the [010] crystal axis. We also noticed that for some modes, such as 259 cm^{-1} mode, the minimum Raman intensity is not along 0° , since there is a small secondary maximum near 0° . This phenomenon, also observed in other layered materials with in-plane anisotropy,^{14, 16, 17, 18} originates from the optical absorption that induces phase mismatch for the Raman tensor elements along different crystal orientations. For the two B_g Raman peaks at $94, 104\text{ cm}^{-1}$, the intensity changes in a period of 90° , with a maximum intensity at 45° and minimum at 0° and 90° . It should be noted that for each mode, such relationship between crystal orientation and Raman intensity remains the same for flakes with different thicknesses. Thus, the combined TEM/Raman measurements unambiguously reveal the relationship between Raman signals and crystal orientation. More importantly, this nondestructive, sensitive and fast anisotropic Raman characterization provides a reliable method to obtain the crystal information of $1T'$ MoTe₂ with various thicknesses.

Figure 2. (a) Optical microscope image of exfoliated $1T'$ MoTe₂ flakes on TEM grid. The arrows labelled by [100]* and [010]* (superscript * indicates the index in reciprocal space) are determined from SAED pattern in (b). (b) SAED pattern from the area shown in (a). The TEM image is shown in the inset. (c) High resolution HAADF-STEM image from the $1T'$ MoTe₂ flake. The inset with red frame is the magnified image from the red rectangle area. [001] atomic projection of the $1T'$ is embedded with red and green spheres representing Mo and Te atoms, respectively. The white framed inset shows the simulated image based on $1T'$ crystal structure, which is consistent with the experimental image. (d) The polarized Raman spectra (633 nm laser excitation) of the same $1T'$ MoTe₂ flake measured with polarization angle from 0° (bottom) to 165° (top) with an interval of 15° . (e) The polar plots of Raman intensity as a function of polarization angles for different Raman modes.

The Raman anisotropy of $1T'$ MoTe₂ flake has remarkable changes under different excitation laser wavelengths. Polarized Raman using three excitation laser wavelengths (532, 633 and 785 nm) were measured on $1T'$ MoTe₂ flakes with various thicknesses on Si/SiO₂ substrates. The flakes that are physically connected were selected to ensure the same crys-

talline orientation. The Raman polar plots of a typical flake of various Raman modes under three laser excitations are summarized in Table 1. Raman polar plots for other flakes with the same crystal orientation are presented in Table S3 and S4. We have noticed several observations from the tables.

The Raman modes show different anisotropy under the same laser excitation wavelengths. For example: $94, 104, 190\text{ cm}^{-1}$ modes always show 90° period (shown with purple fitted curve in Table 1), while all the other modes show 180° period. The reason for such different polar spectra is that, Raman modes have different symmetries: A_g modes show 180° period, and B_g modes show 90° period. Also, for the modes with the same symmetry, the observed anisotropy can be different. For example, for the A_g modes under 532 nm laser, $78, 111, 128, 163, 252\text{ cm}^{-1}$ modes show that maximum intensities are along 0° (shown with violet fitted curve in Table 1), while $259, 265, 279\text{ cm}^{-1}$ modes have their maximum intensities along 90° (shown with orange fitted curve in Table 1).

For the same Raman mode, the Raman anisotropy can change their orientations with changing laser wavelengths. For example, 78 cm^{-1} mode shows the maximum intensity along 0° under 532 nm laser, but along 90° under 633 and 785 nm laser; 128 cm^{-1} mode shows the maximum intensity along 0° under 532 nm laser, but along 90° under 633 nm laser. Some modes change degree of anisotropy with laser wavelengths, and some even become isotropic under certain laser excitations. For example, 163 cm^{-1} shows stronger anisotropy under 633 nm laser than under 532 nm laser, and under 785 nm laser, it shows isotropic Raman intensity. This phenomenon can be attributed to the optical transition selection rule, which will be discussed in detail later. In short, by changing the laser excitation energies, the final or initial electronic states with the different symmetry of the wave functions are selected so as to satisfy the resonance condition. Then the electron-photon matrix elements can have unique polarization dependence even for the same phonon modes that satisfies the group theory. It is noted that the classical theory of Raman tensor cannot explain these phenomena.¹⁹

Table 1. Raman polar plots of a typical flake (5.7 nm thick) of various Raman modes under different incident laser.

mode (cm^{-1})	532 nm	633 nm	785 nm	mode (cm^{-1})	532 nm	633 nm	785 nm
78				190			
94				252			
104				259			
111				265			
128				279			
163							

For flakes with different thicknesses from few-layer to bulk, Raman anisotropy orientations do not change for each

mode. As seen in Table 1 and Table S3 and S4, for the few-layer and bulk flakes, under the same excitation laser wavelengths and for the same Raman modes, the orientations of their Raman intensity polar plots remain the same. This feature can tremendously simplify the method of using polarized Raman to determine crystalline orientation, since the flake thickness does not need to be taken into consideration.

Overall, as seen in Figure 2, Table 1 and Table S3 and S4, polarized Raman measurement should be a sensitive probe to determine the crystalline orientation of 1T' MoTe₂, but some cautions need to be taken on the selection of excitation laser wavelength due to the sensitivity of Raman anisotropy with laser wavelength.

Despite the insensitivity of Raman anisotropy to flake thickness, several Raman features, including peak frequency and intensity ratio, varies with the thickness of 1T' MoTe₂ flakes. We have analyzed various features of Raman spectra of 1T' MoTe₂ under different laser excitations, and found that the A_g modes at 78 and 259 cm⁻¹ as well as the intensity ratio (I(259)/I(252)) can be used for the identification of the thickness of 1T' MoTe₂ sample.

Figure 3. (a) Raman spectra of 1T' MoTe₂ flakes with different thicknesses. Thickness from bottom to top: 3.6, 5.1, 5.8, 6.3, 8.5, 31 nm. The inset shows the zoom-in of 78 cm⁻¹ peak. The spectra were measured under 633 nm laser and along 90° crystal orientation. The spectra intensities are normalized by the corresponding 78 cm⁻¹ mode. (b-d) The frequency change of 78 cm⁻¹ mode with flake thickness under 532, 633, 785 nm laser, respectively. Max. and Min. Int. denote the polarization angle selected for maximum and minimum intensities in the polar plot, respectively. (e) The frequency change of 261 cm⁻¹ mode with flake thickness measured under 633 nm laser with 90° crystal orientation. (f) The thickness dependence of intensity ratio of 259 and 252 cm⁻¹ modes measured under 532 nm laser. Both intensities of (e) and (f) are selected with the polarization for their corresponding maximum intensities, i.e. 90° for 259 cm⁻¹ mode and 0° for the 252 cm⁻¹ mode. (g) Optical image of the flakes (top) and Raman mapping of the 78 cm⁻¹ mode frequency (bottom).

First, the frequencies of 78 and 259 cm⁻¹ modes (under 633 nm laser) exhibit a monotonic redshift when the thickness is

increased (Figure 3a). As shown in Figure 3c, for the few-layer flake (thickness 3.7 nm), the 78 cm⁻¹ mode under 633 nm has the frequency of nearly 80 cm⁻¹, but as the thickness increases to 33.5 nm, its frequency decreases to ~77.7 cm⁻¹. Similarly, under 532 nm laser, the frequency of 78 cm⁻¹ mode changes from 79.5 cm⁻¹ to ~76.9 cm⁻¹ monotonically when thickness increases from 3.7 to 33.5 nm (Figure 3b). Similarly, for 785 nm laser, there is a frequency decreases of 78 cm⁻¹ mode from 80.2 cm⁻¹ to 77.8 (3.7 nm to 33.5 nm thickness) (Figure 3d). For the 261 cm⁻¹ mode with 633 nm laser, the frequency of can decrease from 262.4 to 259.2 cm⁻¹ for thickness increases from 5.2 to 33.5 nm (Figure 3e). Note that the frequencies measured here are chosen for the polarization with the maximum intensity (or minimum intensity) of the modes to minimize the uncertainty of the measured frequency and the subsequent numerical fitting. One possible reason of such a frequency drop with increased flake thickness is the increase of dielectric screening of the long-range Coulomb interaction for an excitation going from few-layer to multi-layer MoTe₂.¹⁹ In particular, the 78 cm⁻¹ mode remains high intensity under variable polarization angles, and the frequency is insensitive to polarization. Thus, the frequency-decreases-rule for 78 cm⁻¹ mode is a good identification for thickness, even for random polarization angle.

Another method to determine the thickness of flakes is using the intensity ratio of 259 to 252 cm⁻¹ modes. We found that the ratio increases with increasing thickness, as shown in Figure 3(f). The ratio is as small as 0.7 for the flake thickness of 3.2 nm, but increases monotonically to 3.5 for the 33.5 nm thick flake. The mechanism that I(259)/I(252) increases with layer thickness is possibly the opposite trend of I(259) measured by x-polarized light and I(252) measured by y-polarized light changing with thickness (see details in SI).

To explain Raman anisotropy, we calculated electronic band structure, optical absorption in the reciprocal space and phonon spectra at the zone-center Γ point of bulk 1T' MoTe₂. The electronic band structure is shown in Figure S1. At the zone-edge X point of the Brillouin zone, there exist several saddle points which will give rise to a Van Hove singularity of electronic joint density of states, or the electron-photon absorption resonance. Indeed, the calculated optical absorption in Figure S2 shows that such an electron-photon resonance appears at or near X point for three laser wavelengths (especially for 532 nm) used in the experiment. Thus, for both inter-valley and intra-valley electronic excitations, the assisting phonon should be sought for at or near Γ point.

The polarized Raman modes can be explained using the group theory and optical transition selection rule^{17,18,20} (see details in SI). Briefly, of the point group of bulk 1T' MoTe₂ is C_{2h}, in which the principal C₂ axis lies in the in-plane y-axis shown in Figure 1a-b. For the linear polarization in the direction of 0° (y direction), the combination of B_g and B_u symmetries, or A_g and A_u symmetries for the initial and photo-excited states are selected (Figure 4a, Table S7). Here for simplicity, we explain the case of B_g and B_u symmetries for the combination of initial and photo-excited state. The full list of the combination of initial and photo-excited states with 0° and 90° (x direction) polarized light are shown in Table S7. For the parallel polarization for incident and scattered light in the Raman measurement, A_g phonon modes can be measured, and 180° period in the polar plots are observed (Figure 4b and c). When the two intermediate states

belong either x or y character, B_g phonon modes can be measured (Table S9), in which we can get 90° period in the polar plots (Figure 4d). By changing laser excitation wavelength, different intermediate states are selected. This is the reason why different polar plots were observed for different excitation laser wavelengths, shown in Table 1.

Figure 4. Selection rule of optical transition. (a) Energy band diagram of bulk 1T'-MoTe₂. The symmetry of energy levels at Γ point are shown, and the polarization of incident and scatter light connecting this energy levels are labelled. (b-c) Two types of A_g Raman modes. (d) B_g Raman mode.

In conclusion, we have demonstrated Raman as a non-destructive and convenient way to determine the crystalline orientation and flake thickness of 1T' MoTe₂. We also perform TEM analysis on 1T' MoTe₂, and successfully correlate it with polarized Raman. We found that the polarized Raman can be effectively used to determine the crystalline orientation of 1T' MoTe₂ flake with thicknesses ranging from few-layer to bulk. Due to the sensitivity of Raman anisotropy with laser excitation wavelengths, special attentions should be paid on the laser wavelength used when determining the crystalline orientation. In addition, the thickness of the flakes can be determined using two ways, the frequency of 78 and 259 cm^{-1} modes, and the intensity ratio of 259 and 252 cm^{-1} mode. The former decreases and the latter increases with increased thickness of the flakes. These experimental observations can be well explained using group theory and DFT calculations. Our work provides insight into the phonon property of the anisotropic material, and paves the way for broad applications of 1T' MoTe₂.

ASSOCIATED CONTENT

Supporting Information

Experimental details and supplementary figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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REFERENCES

- (1)Keum, D. H.; Cho, S.; Kim, J. H.; Choe, D.-H.; Sung, H.-J.; Kan, M.; Kang, H.; Hwang, J.-Y.; Kim, S. W.; Yang, H.; Chang, K. J.; Lee, Y. H. *Nat Phys* **2015**, *11*, 482.
- (2)Deng, K.; Wan, G.; Deng, P.; Zhang, K.; Ding, S.; Wang, E.; Yan, M.; Huang, H.; Zhang, H.; Xu, Z.; Denlinger, J.; Fedorov, A.; Yang, H.; Duan, W.; Yao, H.; Wu, Y.; Fan, S.; Zhang, H.; Chen, X.; Zhou, S. *Nat Phys* **2016**, *12*, 1105.
- (3)Qi, Y.; Naumov, P. G.; Ali, M. N.; Rajamathi, C. R.; Schnelle, W.; Barkalov, O.; Hanfland, M.; Wu, S.-C.; Shekhar, C.; Sun, Y.; Susz, V.; Schmidt, M.; Schwarz, U.; Pippel, E.; Werner, P.; Hillebrand, R.; Forster, T.; Kampert, E.; Parkin, S.; Cava, R. J.; Felser, C.; Yan, B.; Medvedev, S. A. *Nat. Commun.* **2016**, *7*, 11038.
- (4)Cho, S.; Kim, S.; Kim, J. H.; Zhao, J.; Seok, J.; Keum, D. H.; Baik, J.; Choe, D.-H.; Chang, K. J.; Suenaga, K.; Kim, S. W.; Lee, Y. H.; Yang, H. *Science* **2015**, *349*, 625.
- (5)Qian, X.; Liu, J.; Fu, L.; Li, J. *Science* **2014**, *346*, 1344.
- (6)Zhang, Q.; Yang, S. A.; Mi, W.; Cheng, Y.; Schwingenschlögl, U. *Adv. Mater.* **2016**, *28*, 959.
- (7)Pezeshki, A.; Shokouh, S. H. H.; Nazari, T.; Oh, K.; Im, S. *Adv. Mater.* **2016**, *28*, 3216.
- (8)Zhou, L.; Xu, K.; Zubair, A.; Liao, A. D.; Fang, W.; Ouyang, F.; Lee, Y.-H.; Ueno, K.; Saito, R.; Palacios, T.; Kong, J.; Dresselhaus, M. S. *J. Am. Chem. Soc.* **2015**, *137*, 11892.
- (9)Empante, T. A.; Zhou, Y.; Klee, V.; Nguyen, A. E.; Lu, I. H.; Valentin, M. D.; Naghibi Alvarar, S. A.; Preciado, E.; Berges, A. J.; Merida, C. S.; Gomez, M.; Bobek, S.; Isarraraz, M.; Reed, E. J.; Bartels, L. *ACS Nano* **2017**, *11*, 900.
- (10)Zhou, L.; Zubair, A.; Wang, Z.; Zhang, X.; Ouyang, F.; Xu, K.; Fang, W.; Ueno, K.; Li, J.; Palacios, T.; Kong, J.; Dresselhaus, M. S. *Adv. Mater.* **2016**, *28*, 9526.
- (11)Zhou, L.; Xu, K.; Zubair, A.; Zhang, X.; Ouyang, F.; Palacios, T.; Dresselhaus, M. S.; Li, Y.; Kong, J. *Adv. Funct. Mater.* **2017**, *27*, 1603491.
- (12)Duerloo, K.-A. N.; Li, Y.; Reed, E. J. *Nat. Commun.* **2014**, *5*, 4214.
- (13)Song, S.; Keum, D. H.; Cho, S.; Perello, D.; Kim, Y.; Lee, Y. H. *Nano Lett.* **2016**, *16*, 188.
- (14)Beams, R.; Cançado, L. G.; Krylyuk, S.; Kalish, I.; Kalanyan, B.; Singh, A. K.; Choudhary, K.; Bruma, A.; Vora, P. M.; Tavazza, F.; Davydov, A. V.; Stranick, S. J. *ACS Nano* **2016**, *10*, 9626.
- (15)Brown, B. *Acta Crystallographica* **1966**, *20*, 268.
- (16)Ribeiro, H. B.; Pimenta, M. A.; de Matos, C. J. S.; Moreira, R. L.; Rodin, A. S.; Zapata, J. D.; de Souza, E. A. T.; Castro Neto, A. H. *ACS Nano* **2015**, *9*, 4270.
- (17)Ling, X.; Huang, S.; Hasdeo, E. H.; Liang, L.; Parkin, W. M.; Tatsumi, Y.; Nugraha, A. R. T.; Puzetky, A. A.; Das, P. M.; Sumpter, B. G.; Geohegan, D. B.; Kong, J.; Saito, R.; Drndic, M.; Meunier, V.; Dresselhaus, M. S. *Nano Lett.* **2016**, *16*, 2260.
- (18)Huang, S.; Tatsumi, Y.; Ling, X.; Guo, H.; Wang, Z.; Watson, G.; Puzetky, A. A.; Geohegan, D. B.; Kong, J.; Li, J.; Yang, T.; Saito, R.; Dresselhaus, M. S. *ACS Nano* **2016**, *10*, 8964.
- (19)Shim, G. W.; Yoo, K.; Seo, S.-B.; Shin, J.; Jung, D. Y.; Kang, I.-S.; Ahn, C. W.; Cho, B. J.; Choi, S.-Y. *ACS Nano* **2014**, *8*, 6655.
- (20)Saito, R.; Tatsumi, Y.; Huang, S.; Ling, X.; Dresselhaus, M. S. *J. Phys.: Condens. Matter* **2016**, *28*, 353002.